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A new band system of the MgBr molecule

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Abstract An electronic emission spectrum of magnesium monobromide molecule, excited in high temperature furnace, has been photographed in the $\lambda\lambda$ 3600 – 4050 Å region at reciprocal linear dispersion of 7 3 Å/mm The study reveals the presence of a new band system, B – X in $\lambda\lambda$ 3600 – 3800 Å region About 16 single headed bands, degraded to higher wavelength side, have been attributed to this system The vibrational analysis performed suggests that the system arises from the ground state involving transition $B^2\Sigma - X^2\Sigma$ The vibrational constants have been determined for the relevant states

Keywords Thermal emission technique, Spectrum of the MgBr molecule Vibrational analysis

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1. Introduction

Magnesium monobromide molecule (MgBr) has been the subject of a large range of spectroscopic studies [1-8]. Several optical absorption and emission studies were concerned with the ground and low-laying excited states of the neutral species, leading to information about energetics, vibrational frequencies, equilibrium bond lengths and dissociation energies Six electronic transitions have been identified, all involving the ground electronic states *viz.* $A^2\Pi - X^2\Sigma$ ($\lambda\lambda$ 3659 – 4033 Å), $C^2\Sigma - X^2\Sigma$ ($\lambda\lambda$ 2540 – 2720 Å) $D^2\Sigma - X^2\Sigma$ ($\lambda\lambda$ 2085 – 2125 Å), $E^2\Pi - X^2\Sigma$ ($\lambda\lambda$ 2060 – 2125 Å), $F^2\Sigma - X^2\Sigma$ ($\lambda\lambda$ 2035 – 2075Å) and $G^2\Pi - X^2\Sigma$ ($\lambda\lambda$ 2045 – 2080 Å). In addition Yamdagni [9] photographed nine entirely new bands in the region $\lambda\lambda$ 3660 – 3790 Å in absorption but due to weak and diffuse bands he could not propose any vibrational assignments The rotational study of the $A^2\Pi - X^2\Sigma$ band system has been performed by Walker and Gerry [10] and Hirao *et al*

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[11] using high resolution Fourier Transform Spectrometer and reported improved rotational constants

While six band systems have been reported for the MgBr molecule, the study of MgI molecule in emission as well as in absorption has disclosed the presence of four systems *viz* A, B, C, and D in the $\lambda\lambda$ 3600 – 4000 Å region The study of the MgCl molecule in thermal emission by Uttam *et al* [12] has revealed the presence of a large number of new bands in the region $\lambda\lambda$ 3660 – 3790 Å Since MgCl, MgBr, MgI molecules are isovalent molecule, similar band systems for the MgBr molecule can be reasonably expected Since thermal emission is a low energy excitation, the spectra involving much higher energy states generally do not appear Thermally excited emission spectra are found to be almost free from atomic lines In most cases, the spectrum obtained by this method involves the ground state and the lower electronic states of the system Therefore we decided to examine the spectrum of MgBr molecule using high temperature graphite furnace

We have been able to record the thermal emission spectrum of the MgBr in the $\lambda\lambda$ 3600–4000 Å region using a high temperature vacuum graphite furnace Here we report the first vibrational analysis of a new system $B^2\Sigma - X^2\Sigma$

2. Experimental details

A small quantity of pure solid magnesium bromide (BDH, 98%) was put into the experimental tube of the Saha's high temperature graphite furnace [13] After evacuation the furnace chamber was filled with argon gas at about a pressure of 500 Torr to prevent a rapid effusion of molecular vapour from the open ends of the carbon tube A temperature of about 2400°C was raised and the spectrum was recorded in first order of 2-m plane grating spectrograph equipped with a grating blazed at λ 5600 Å and total lines ruled 45500 at a reciprocal linear dispersion of 7 3 Å/mm An exposure time of about 12 min was found sufficient to record a good spectrogram on ILFORD 400 ASA black and white film in first order The iron arc spectrum was recorded for calibration lines The spectra were measured on an Abbe Comparator with the least count of 0 0001 cm

3. Results and discussion

The thermal emission spectrum of the MgBr molecule has been photographed in the $\lambda\lambda$ 3600 – 4000 Å region A part of the spectrum is reproduced in Figure 1 The A – X system has been recorded in $\lambda\lambda$ 3659 – 4033 Å region along with some new bands The spectrum is free of atomic lines Contrary to the suggestion of Yamdagni [9], the bands could be seen in the spectrogram and are measured accurately About 16 single headed bands, degraded to longer wavelength side, have been recorded in the region $\lambda\lambda$ 3600 – 3800 Å The observed bands has been classified into $\Delta v = 0, \pm 1, \pm 2$ sequences of a new system B – X The bands of B–X system can be described by the expression

$$\nu = \nu_e + \omega_e'\left(v' + \frac{1}{2}\right) - \omega_e x_e\left(v' + \frac{1}{2}\right)^2 - \omega_e''\left(v'' + \frac{1}{2}\right) + \omega_e x_e''\left(v'' + \frac{1}{2}\right)^2$$

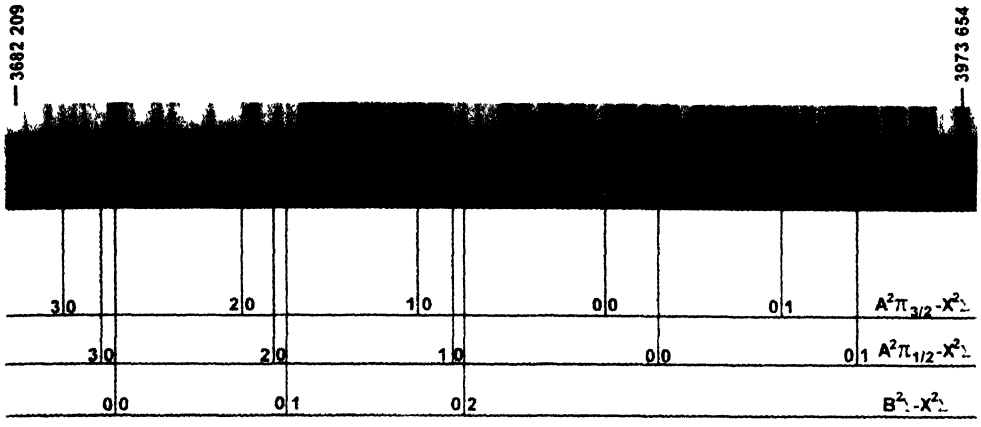

Figure 1. Thermal emission spectrum of MgBr molecule at a reciprocal linear dispersion of 7 3 A / mm

The following vibrational constants have been determined from the vibrational analysis using Deslandre Table

$$\nu_{00} = 26924\ 0 \qquad \omega'_e = 357, \qquad \omega_e x'_e - 2\ 0\ \text{cm}^{-1}$$

$$\omega''_e - 374\ 2, \qquad \omega_e x''_e = 1\ 2\ \text{cm}^{-1}$$

Table 1. Band Head Data of the $B^2\Sigma - X^2\Sigma$ System of the MgBr Molecule

S No	ν_{cal} (cm^{-1})	ν_{obs} (cm^{-1})	(v', v'')	Intensity
1	26182 8	26182 0	(0,2)	2
2	26168 8	26167 3	(1,3)	1
3	26552 2	26553 0	(0,1)	3
4	26535 8	26534 7	(1,2)	2
5	26517 8	26516 7	(2,3)	1
6	26924 0	26924 0	(0,0)	5
7	26905 2	26904 2	(1,1)	4
8	26884 8	26883 9	(2,2)	3
9	26862 8	26862 3	(3,3)	2
10	26839 2	26840 2	(4,4)	1
11	26814 0	26813 7	(5,5)	1
12	27277 0	27279 0	(1 0)	2
13	27254 2	27255 1	(2 1)	2
14	27229 8	27228 7	(3,2)	1
15	27203 8	27203 4	(4,3)	1
16	27626 0	27626 5	(2,0)	1

The band head data, visual estimates of intensities and their vibrational assignment have been collected in Table 1 The maximum value of the difference between observed and calculated is ± 2 cm^{-1}

The occurrence of new bands together with known MgBr bands, and the complete absence of any identifiable impurity spectra, suggests that the new bands belong to the MgBr The lower state vibrational constants determined here agree with those reported by Puri and Mohan [7] and Rao *et al* [8] for the ground state of the MgBr molecule This confirms that the present system of bands is indeed due to the MgBr molecule, and that the transition terminates on the ground state

The B – X system of the three MgX molecules (X = F, Cl, I) investigated earlier appears in the regions MgF ($\lambda\lambda$ 2630 – 2742 Å), MgCl ($\lambda\lambda$ 2666 – 2733 Å), MgI ($\lambda\lambda$ 3850 – 4010 Å) Thus the occurrence of the MgBr brands in the $\lambda\lambda$ 3600 – 3800 Å region is quite in line with the general trend The (0, 0) band in the case of this system for the MgF, MgCl, MgI molecules lies at λ = 2689 Å, λ = 2697 0 Å and λ = 3904 5 Å respectively It can be seen that the shift of the B – X system as a whole and the respective (0,0) bands, to the ultraviolet is quite general Similar behaviour is shown by their ground state vibrational frequencies also The summary of the vibrational constants of all the observed systems of the MgBr molecule and shown in Table 2

Table 2 Vibrational Constants of the MgBr Molecule (cm^{-1})

System	Region (Å)	ν_{00}	ω_e	$\omega_e'x_e'$	ω_e	$\omega_e x_e$	Remarks
$A^2\Pi_{1/2}$ $X^2\Sigma$	$\lambda\lambda$ 3659–4033	25775 0	393 9	2 04	374 14	1 47	Ref [7]
$A^2\Pi_{3/2} - X^2\Sigma$	$\lambda\lambda$ 3659–4033	25885 0	394 0	2 00	373 4	1 20	Ref [7]
$B^2\Sigma - X^2\Sigma$	$\lambda\lambda$ 3600–3800	26924 0	357 0	2 00	374 2	1 2	*
$C^2\Sigma - X^2\Sigma$	$\lambda\lambda$ 2540–2720	39285 9	271 9	5 20	373 2	1 34	Ref [6]
$D^2\Sigma - X^2\Sigma$	$\lambda\lambda$ 2085–2125	47499 9	386 6	0 63	375 2	1 80	Ref [8]
$E^2\Pi_{1/2}$ $X^2\Sigma$	$\lambda\lambda$ 2060–2125	47828 4	400 1	1 28	375 0	1 74	Ref [8]
$E^2\Pi_{3/2} - X^2\Sigma$	$\lambda\lambda$ 2060–2125	47998 6	400 1	1 28	375 0	1 74	Ref [8]
$F^2\Sigma - X^2\Sigma$	$\lambda\lambda$ 2035–2075	48575 5	408 2	1 03	376 1	2 33	Ref [8]
$G^2\Pi_{3/2} - X^2\Sigma$	$\lambda\lambda$ 2045–2080	48819 9	421 4#	–	377 2	2 16	Ref [8]

* Constants suggested by authors, # $\Delta G_{1/2}$ value

The normal state electronic configuration of Mg and Br atoms are given by

$$_{12}Mg \quad 1s^2, 2s^2 2p^6, 3s^2 \text{ -------- } {}^1S_0$$

$$_{35}Br \quad 1s^2, 2s^2 2p^6, 3s^3 3p^6 3d^{10}, 4s^2 4p^6 \text{ -------- } {}^2P_{3/2}$$

Considering the separated atom model, the ground state of magnesium is $^1S_0$ while bromine has $^2P_{3/2}$ The resulting molecular electronic states are $^2\Pi$, $^2\Sigma$ The ground state for MgBr molecule has been established as a $^2\Sigma$ [9] arising from electronic configuration $(w\pi)^4\ (x\sigma)^1$ Thus the optically allowed features of spectra (single headed, sharp, and well developed bands) support the assignment of B – X system to the transition $^2\Sigma - ^2\Sigma$ This conclusion is analogous to the B – X system of isovalent molecules like MgF and MgI [9].

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